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⑷ Improved gas barrier structure for pneumatic articles.

⑷ A gas barrier structure for pneumatic articles, comprising a gas barrier film having low gas permeability, in which the gas barrier film is laminated between and bonded to two vulcanizable elastomeric surface layers and is a non-elastomeric polymeric layer that has an air permeability of no more than  $0.05 \times 10^{-10}$  cc-cm/cm<sup>2</sup>-cmHg-sec at 23 °C, and the said structure incorporated into a tubeless pneumatic vehicle tire as the tire innerliner, are disclosed.

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## IMPROVED GAS BARRIER STRUCTURE FOR PNEUMATIC ARTICLES.

This invention relates to gas barrier structures for pneumatic articles, such as innerliners for tubeless pneumatic tires.

In most pneumatic articles, for instance, blimps or tires for vehicles or aircraft, weight is an important consideration. Gas barrier structures for such articles, are conventionally based on butyl rubber or a halobutyl rubber, typically chlorobutyl. In order to give satisfactory air-pressure retention, the thickness of a halobutyl rubber-based gas barrier, such as the tire innerliner for a passenger car or light truck, has to be on the order of about 1.5 mm (60 mils). Such a liner has an air permeance of about 230 cc/m<sup>2</sup>/atm/day at 65 °C. For a good quality 38 cm (15 in) passenger-car tire the liner weighs about 1.13 kg (2.5 lbs), which is about 10% of the total weight of the tire.

70 Pneumatic tires typically comprise several plies of reinforced rubber permanently laminated by molding and curing, the innerliner (also called the liner or liner ply) being the inner-most layer and having lower air-permeability than the rubber employed in the other layers.

In the case of vehicles, the fuel economy of the tires of a vehicle is primarily determined by its rolling resistance. When a vehicle is running, all of the components in the tires are flexing at a high frequency. A 75 significant amount of energy is lost by the heat generated in the tire due to hysteresis, which is determined by the nature and the mass of the tire components. Therefore, it is highly desirable to achieve a reduction in the mass of any of the components, while maintaining its functional performance, to reduce its share of the energy loss and result in an improvement of fuel economy and tire performance.

Tire rolling resistance is also affected by its inflation pressure. An increase in tire pressure would also 20 reduce rolling resistance. However, with a halobutyl rubber innerliner, such a higher pressure can be maintained only by a thicker and heavier liner. The added weight of a thicker liner would increase the hysteresis loss, which would more than offset the gain from the higher air pressure for improving fuel economy that would be achieved by improving the air barrier property of the innerliner.

While butyl and halobutyl rubbers have the best air-barrier characteristics among elastomers, other 25 materials not considered to be elastomers possess much better air-barrier properties. For example, films made of thermoplastic polymers, such as vinylidene chloride based polymers (PVDC) and ethylene-vinyl alcohol copolymers (EVOH), have air permeabilities that are only a fraction of a percent of the permeability of a typical butyl rubber film of the same thickness. Although these barrier materials are well known in applications such as food packaging that benefit from low air-permeability, they have not been successfully 30 used in the construction of vehicle tires or other articles having similar functionality and requirements for production.

Using those known barrier materials in tire construction, for instance, would be considered to be impractical for several reasons. Being thin films, handling them without creating wrinkles or other defects is difficult, and since the preferred barrier materials are thermoplastics, they might be expected to melt or 35 degrade at tire-curing temperatures, which may range from 120 to 200 °C. Also, normal service on a vehicle might be expected to distort such non-elastomeric films beyond their elastic limits as indicated by their manufacturers' elongation-to-break specifications.

According to the invention, a gas barrier structure for pneumatic articles, comprising a gas barrier film having low gas permeability, is characterized in that the gas barrier film is laminated between and bonded 40 to two vulcanizable elastomeric surface layers and is a non-elastomeric polymeric layer that has an air permeability (P) of no more than  $0.05 \times 10^{-10}$  cc-cm/cm<sup>2</sup>-cmHg-sec (0.05 Barrer or 16.6 cc-mil/100 in<sup>2</sup>-atm-day) at 23 °C.

The gas barrier structures according to the invention combine substantially higher levels of gas-pressure retention with a substantial reduction in weight per unit area, as compared to conventional butyl or 45 halobutyl rubber innerliner materials. The air permeability of butyl or halobutyl rubber (the best of the standard materials for current commercial tire innerliners) is about  $0.5 \times 10^{-10}$  cc-cm/cm<sup>2</sup>-cmHg-sec, so that layer of the non-elastomeric polymeric barrier layer material one micrometer (1 mil) thick in the gas barrier structure of this invention may be equivalent in air permeability to ten or more times that thickness of butyl rubber.

50 Incorporation of the thin non-elastomeric polymeric layer film barrier material into a laminate with the rubber surface layers overcomes in several ways the perceived disadvantages of barrier materials that are well known in such applications as food packaging. Firstly, it creates a gas barrier structure of increased bulk and body as compared to a layer of the non-elastomeric film barrier material, which facilitates handling without creating wrinkles or other defects.

Secondly, the rubber surface layers protect and preserve the thin film barrier materials, which are

thermoplastic materials that may soften or even melt at curing temperatures. The bonding to the rubber surface layers maintains the dimensional integrity of the thermoplastic material even under those conditions, restraining any tendency to flow and permitting re-solidification without dimensional change at a lower temperature.

- 5 Thirdly, rubber surface layers tend to insulate the thermoplastic material from the higher curing temperatures, thus minimizing thermal degradation of the thermoplastic, a particular advantage in the case of PVDC polymers. In the case of an EVOH barrier layer, the rubber layers protect the barrier layer from moisture, to which the EVOH polymers are sensitive.

Finally, the bonding to the rubber surface layers overcomes the disadvantages caused by the difference 10 in elasticity between the elastomeric materials and the non-elastomeric films. Rubber, as is well known, is a highly elastic material, and can be elongated by several hundred percent without exceeding its elastic limit. This quality is the principal reason that rubber is used in tires, since it allows a tire to withstand the extremely rough treatment that it receives in everyday usage. The non-elastomeric barrier films, by contrast, have relatively low elastic limits. Either normal service on a vehicle or inflation may distort the film 15 beyond its elastic limit. When the film is bound between the rubber layers, the barrier layer can be stretched beyond its normal elastic limit along with the rubber surface layers. In that case, when the laminate returns to its original dimensions, the barrier material is forced into a folded, sinusoidal configuration with the interior surface of the rubber layers following the folds in the barrier material and the integrity of the innerliner structure is maintained. The gas barrier film is also protected from abrasion and breakage 20 by being enclosed between the rubber layers.

For non-tire applications where a thin rubbery material with high gas barrier property is required, the gas barrier structures have adequate flexibility and extensibility to meet the requirements for inflation and use, and are able to withstand the conditions required for vulcanization.

For use as vehicle-tire innerliners, the structures according to the invention have adequate flexibility and 25 extensibility to meet the requirements in use of tubeless pneumatic tires and are able to withstand the conditions required for the fabrication and vulcanization of the tires, including ensuring the bonding of the outer elastomeric surface layer to the other rubbers used in the adjacent layer.

The gas barrier material can be selected from a wide variety of non-elastomeric materials as long as the material has the specified air permeability limits (no greater than  $0.05 \times 10^{-10}$  cc-cm/cm<sup>2</sup>-cmHg-sec 30 (16.6 cc-mil/100 in<sup>2</sup>-atm-day) at 23 °C).

Examples of thin film barrier materials that meet the above mentioned requirements are as follows:

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Materials	Melting and Softening Points (°C)	GAS PERMEABILITY, IN BARRIERS, AT 23°C.				
		O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	He	Air(Calc.)
EVAL <sup>b</sup> EP-F EVOH	-181 <sup>(a)</sup>	6.02x10 <sup>-5</sup>	6.02x10 <sup>-6</sup>	1.93x10 <sup>-4</sup>	0.06	1.81x10 <sup>-5</sup>
" EP-H "	-175	1.81x10 <sup>-4</sup>	2.41x10 <sup>-5</sup>	4.04x10 <sup>-3</sup>	0.1	5.42x10 <sup>-5</sup>
" EP-E	-164	5.48x10 <sup>-4</sup>	4.82x10 <sup>-3</sup>	1.29x10 <sup>-3</sup>	0.14	1.51x10 <sup>-4</sup>
Saran <sup>b</sup> 5253 PVDC	-165 <sup>(a)</sup>	9.04x10 <sup>-4</sup>	7.23x10 <sup>-5</sup>	1.99x10 <sup>-3</sup>	0.16	2.41x10 <sup>-5</sup>
Barex <sup>b</sup> 210 Nitrile	-170 <sup>(a,b,c)</sup>	4.82x10 <sup>-3</sup>		6.63x10 <sup>-3</sup>		
Nylon 6 (a)	-216	1.57x10 <sup>-2</sup>	5.42x10 <sup>-3</sup>	2.83x10 <sup>-3</sup>		7.47x10 <sup>-3</sup>
Amorphous nylon	-200 <sup>(c)</sup>	1.20x10 <sup>-2</sup>				
PET polyester	-258 <sup>(b)</sup>	3.01x10 <sup>-2</sup>				
For comparison:						
Natural rubber <sup>(e)</sup>		23.2	8.05	131.1	31.2	11.1
Butyl rubber <sup>(e)</sup>		1.30	0.33	5.16	8.42	0.52
Polyepichlorohydrin <sup>(e)</sup>		0.31	0.047	3.41	1.74	0.1
Oriented PP <sup>(b)</sup>		0.98				

(a) Data from Technical Bulletin No. 110, "Gas Barrier Properties of Eval Resins," p. 2, Table 1, Kuraray Co., Tokyo.

(b) Data from "Packaging Encyclopedia & Yearbook 1985," pp. 64F-65, Cahners Publishing Co., Denver, CO.

(c) Data from Technical Bulletin E-73974, "Selar PA 3426 Barrier Resin," DuPont Company, Wilmington, DE.

(d) Modern Plastics Encyclopedia.

(e) Data from "Rubber Handbook," p. 284, Table 6, R. T. Vanderbilt Co., Norwalk, CT.

Vinylidene-chloride-based polymers applicable in this invention as the gas-barrier material can be a copolymer of vinylidene chloride (VDC) with one or more comonomers including, but not limited to, vinyl chloride, acrylonitrile, acrylates, methacrylates, and the acrylic acids. Some of these materials are listed above, including those sold under the trademark "Saran" by Dow Chemical Company, Midland, Michigan. The best barrier properties are achieved with higher concentrations of VDC, while better flexibility is usually associated with a lower VDC content in the polymer. Preferred are polymers having 60 to 95% VDC.

Ethylene-vinyl-alcohol copolymers useful as the gas-barrier material are saponification products of ethylene-vinyl acetate copolymers. Better barrier properties are achieved with higher vinyl alcohol content, i.e., lower ethylene content and higher degree of saponification of the vinyl acetate moieties in the copolymer. Some of these materials are listed above and are sold under the trademark "EVAL" by Kuraray Co., Ltd., Osaka, Japan. Preferred polymers contain less than 50 mole % ethylene and are more than 90% saponified.

Both the ethylene-vinyl alcohol copolymer and the vinylidene chloride based polymers are thermoplastic, film-forming polymers. Both are amenable to extrusion at reasonably low working temperatures. Preferably, the material used for the rubber surface layers of the laminate is calendered to the desired thickness and laminated to both sides of the thermoplastic polymer film to give an three-layer laminated sheet. Alternatively, the three-layer laminated sheet containing the barrier material layer may be prepared by conventional co-extrusion, in which all three layers are extruded simultaneously through a single die having three extrusion orifices.

Conventional additives, such as plasticizers, modifying resins, processing aids, etc. can be included therein. A processing aid such as a glycol or polyhydroxyl compound of 2-10% based on the weight of the copolymer is useful when the copolymer is an extrusion grade ethylene-vinyl alcohol copolymer.

The materials used for the rubber surface layers of the laminate can be any conventional elastomer, including thermoplastic elastomers with appropriate compounding. It is permissible, and may even be desirable, to apply rubber layers of different compositions to the opposite faces of the barrier layer, possibly for reasons of economics, availability, suitability for fabrication, or meeting other functional requirements. For tire innerliners the composition of the outer rubber surface layer at least must be selected to provide strong adhesion to the inner layer of the carcass as well as to the barrier layer.

Thermoplastic elastomers (TPE's) may be used for the rubber surface layers. The TPE's are more

convenient to extrude into thin films than are the conventional elastomers that may also be used, such as SBR's or butyl and natural rubbers. However, the conventional elastomers are easier to calender. For tire innerliners, any TPE or conventional elastomer or a blend of both that gives the necessary adhesion to the carcass ply of the tire and the barrier material can be used to make the surface layers.

5 Styrene block-copolymer TPE's such as those sold under the trademark "Kraton" by Shell Chemical Company, polyolefin TPE's such as "Santoprene" by Monsanto Company, and polyester TPE's such as "Hytrell" by DuPont are examples of TPE's that work well.

10 The thermoplastic nature of TPE's may be retained for applications that do not involve exposure to temperatures high enough to cause softening. However, if the gas barrier structures according to the invention are to be used as tire innerliners, and in any case if conventional elastomers are used, appropriate vulcanizing agents should be incorporated in the elastomer surface layers. The vulcanizing agents will make TPE surface layers used in tire innerliners more adaptable for conventional tire making processes and improve adhesion to the inner layer of the carcass when the tire is cured. In any case, the air permeability of the non-elastomeric materials cited above for the polymeric layer is not affected by vulcanization.

15 The elastomer surface layers may of course be further compounded with reinforcing fillers such as carbon black, tackifying agents, plasticizers, and other well known modifiers to improve the physical properties of the surface layers.

20 Preferably, the bonding between adjacent layers in the laminated structure will be sufficiently strong to prevent delamination when the structure is tensile-stretched to 100 percent elongation in any direction. In many combinations of the gas barrier film and the material of the elastomeric surface layers, that degree of adhesion can be developed by the appropriate compounding of the elastomeric rubber material or the polymeric material of the non-elastomeric layer or both, or by a surface treatment of either or both of the layers.

25 Preferably, that degree of adhesion is achieved by incorporating in the material of the surface layers appropriate phenolic resins, which include both the heat-reactive types that are used as curing resins for butyl rubber and other elastomers (such as the "SP 1044" and "SP-1045" resins available from Schenectady Chemicals Co., Schenectady, New York) and the non-reactive type of phenolic tackifying resins, such as the "SP-1077" resins also available from Schenectady Chemicals Co.

30 For some combinations of layer materials, an adequate degree of adhesion between the rubber surface layers and the gas barrier film material layer can be achieved by applying an adhesive or tie layer between the layers. For a PVDC barrier layer and the rubber surface layers, a copolymer of ethylene and ethyl acrylate or other acrylate or methacrylate monomer (EEA resin) may be used in the tie layer. Preferably, the tie layer is a blend of EEA resin and styrene-isoprene or styrene-butadiene thermoplastic elastomers or the hydrogenated products thereof. The blending ratio can be in the range of about 10 to 90% of EEA, 35 preferably between about 25 and 75% of EEA. The most preferred EEA resin contains about 70% ethylene.

For an EVOH barrier layer and the rubber surface layers, a blend of maleic anhydride grafted polypropylene and styrene-isoprene or styrene-butadiene thermoplastic elastomer or the hydrogenated products thereof may be used for the tie layer. The blending ratio can be in the range of about 5 to 95%, 40 preferably from 10 to 50%, of the grafted polypropylene. The maleic anhydride content of the grafted polypropylene is preferably from about 0.05 to 5%, more preferably 0.1 to 4%.

The improved properties of tires the gas barrier structures according to the invention are demonstrated by the following examples. Parts and percentages are by weight unless otherwise specified.

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#### Example 1

An improved innerliner in accordance to this invention was fabricated by coextruding a 5-layer sheet in ABCBA order of lamination. Layer A, the surface layer, had the following ingredients:

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5	Block copolymer TPE <sup>1</sup>	100.0 parts
10	Stearic acid	1.0 parts
	Hydroquinoline antioxidant <sup>2</sup>	1.0 parts
	Zinc oxide	1.5 parts
	Carbon black N550	20.0 parts
	Hydrocarbon Resin <sup>3</sup>	20.0 parts
	Vulcanization accelerator <sup>4</sup>	0.3 parts
	vulcanizing agent <sup>5</sup>	2.0 parts
	Sulfur	0.3 parts

1. Kraton 1117 by Shell Chemical Co.  
 2. Agerite Resin D by R. T. Vanderbilt Co.  
 3. Piccopale 100 by Hercules.  
 4. Santocure by Monsanto Company.  
 5. Sulfasan R by Monsanto Company.

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The mixture was prepared in a manner standard to the rubber industry, using a Banbury mixer, a 2-roll mill, and other auxiliary equipment.

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Layer B, a tie layer, had the following ingredients:

Hydrogenated styrenic block TPE	60.0 parts
EEA Resin (DPD-6169 from Union Carbide)	40.0 parts

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Pellets of both these components were thoroughly blended in a V-blender.

Component C is an extrusion-grade PVDC resin (available under the registered trademark Saran from Dow Chemical Co.).

These three components were fed from separate extruders into a 5-layer feed block where components

30 A and B were each split into two streams. Thereafter, the layers, still maintaining their identity, were extruded through a common die into the 5-layer composite sheet (A,B,C,B,A), which was quenched on a chill roll. The thickness of the layers was controlled by adjusting the throughput rate of the individual extruders feeding into the feed block. The resultant layer thicknesses were 7, 1, 2, 1, and 7 mils respectively for A, B, C, B, and A.

35 The sheet was found to have excellent air barrier properties. Its air permeance is 155 cc/m<sup>2</sup>/atm/day, which is significantly lower than the 194 cc/m<sup>2</sup>/atm/day air permeance of a typical commercial chlorobutyl rubber based innerliner at 60 mils thick. The sheet was rubbery and stretchable. It was found that after being stretched to 200% elongation, and released, the sheet specimen substantially recovered its original dimensions. More importantly, the air permeability of the sheet had not changed. Upon examining the 40 cross-section of the specimen under a scanning electron microscope, it was found that the barrier layer had been forced into a folded, sinusoidal, or a "micro-corrugated" configuration with the interior surface of the rubber skins following the contour of the barrier layer and maintaining the integrity of the laminate structure.

The laminate was used as a direct replacement of the conventional innerliner of a tubeless 15-inch light truck tire in a standard tire making operation. It exhibited excellent tack to the carcass ply, and there was no 45 difficulty through the entire tire-making process. The resultant tire (tire A) satisfactorily passed the standard air pressure retention test by retaining more than 98% of the 310 kPa (45 psig) pressure in a constant (23 °C) temperature room for 2 weeks. A commercial tire (tire C) made with the standard liner was used as the control. It also showed a 98% pressure retention over the same 2-week period. The innerliner sheet of this invention for the 15 inch light truck (tire A) weighed 0.43 kg (0.95 pounds) while the standard halobutyl interliner of the conventional 15 inch commercial tire (tire C) weighed 1.35 kg (2.97 pounds).

50 Separately, the sheet was modified to give a micro-corrugated barrier layer by mechanically stretching it to 200% elongation and then relaxing it, and was used to make tires (tire B) as above. The tires were found to retain 99% of the 45 psig air pressure over the 2-week period.

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#### Example 2

The liner in accordance to this invention of a three layer laminated sheet of A-C-A structure was prepared.

Component A is the surface layer which had the following ingredients::

5	Block copolymer TPE <sup>1</sup> Stearic acid Age Rite Resin D Zinc oxide Carbon black Piccopale 100 Resin Phenolic resin, heat-reactive <sup>2</sup> Phenolic resin, non-heat-reactive <sup>3</sup> Santocure Sulfasan R Sulfur	100.0 parts 1.5 parts 1.0 parts 1.5 parts 25.0 parts 15.0 parts 5.0 parts 3.0 parts 0.3 parts 4.0 parts 0.3 parts
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- 1. Kraton 1117
- 2. Schenectady SP-1045 by Schenectady Chemicals Company.
- 3. Schenectady SP-1077 by Schenectady Chemicals Company.

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The mixture was compounded in a manner standard to the rubber industry, using a Banbury mixer, a 2-roll mill, and other auxiliary equipment.

Component C, the barrier layer, is an extrusion grade ethylene-vinyl alcohol (EVOH) copolymer resin (EVAL-G from the Kuraray Co., Ltd.), further modified with 4% of ethylene glycol based on the weight of the EVOH resin to improve processibility.

These two components were coextruded from separate extruders through a 3-layer feed block. Component A was split into two streams to form the surface layers sandwiching the barrier layer C. Thereafter, the layers converged but maintained their identity, and were extruded through a common die set at the desired die gap clearance into a 3-layer composite sheet. The thickness of the layers was controlled by adjusting the throughput rate of the individual extruders. The resultant layer thickness was 0.229, 0.025, and 0.229 mm (9, 1, and .9 mils) respectively for A, C, and A.

The sheet was found to have excellent air barrier properties. Its air permeance is 49.6 cc/m<sup>2</sup>/atm/day at 65.5 °C which is much lower than that of a typical premium grade commercial innerliner of 0.140 mm (55 mil) halobutyl rubber at 210.8 cc/m<sup>2</sup>/atm/day. A sample of the sheet was stretched to 150% elongation, which far exceeds the elongation to be endured by the innerliner in tire-making process or during the use of tires. After the stress was released, the sheet substantially recovered its original overall dimensions. The air permeance was found to be 57.4 cc/m<sup>2</sup>/atm/day at 65.5 °C., thus ensuring that excellent air barrier properties will be achieved with this material as tire innerliner.

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### Example 3

45 An innerliner similar to that in Example 2 of a three layer laminated sheet of A-C-A structure was prepared.

Component A is the surface layer and had the following ingredients:

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5	Block copolymer TPE (1)	100.0 parts
	Stearic acid	1.5 parts
	Age Rite Resin D	1.0 parts
	Zinc oxide	1.5 parts
	Carbon black	35.0 parts
	Piccopale 100 Resin	15.0 parts
10	Phenolic resin, heat-reactive (2)	5.0 parts
	Phenolic resin, non-heat-reactive (3)	3.0 parts
	Santocure	0.3 parts
	Sulfasan R	3.0 parts
	Sulfur	0.3 parts

(1) Kraton 1117.

(2) Schenectady SP-1045.

15 (3) Schenectady SP-1077.

The mixture was compounded in the standard manner as described before.

20 Component C, the barrier layer, was a 0.8 mil thick extruded film of an ethylene-vinyl alcohol (EVOH) copolymer resin (EVAL-E from the Kuraray Co.).

Component A was calendered on a 3-roll calender to about 12 mils in thickness and laminated to both sides of component C to give the A-C-A three layer laminated sheet. The over-all thickness was about 25 mils.

25 The air permeance of the 25-mil sheet was 51.3 cc/m<sup>2</sup>/atm/day at 150° F (65.5° C), which is only one-fourth of that of a 55-mil premium grade halobutyl rubber inner liner at 210.8 cc/m<sup>2</sup>/atm/day under the same testing conditions. The halobutyl innerliner for a 13 inch tubeless tire weighed 2.02 pounds while the same size innerliner of the instant invention weighed only 0.73 pounds representing a 63.8% weight reduction.

30 The sheet was successfully used as a direct replacement of the conventional innerliner of a 13-inch tubeless passenger car tire. The resultant tire passed the standard air pressure retention test by retaining 99% of the 45 psi. initial pressure over the two week test period.

While multi-layer coextrusion and calendering were used to fabricate the innerliner in the above examples, they are not the only methods applicable. Extrusion coating, lamination and other techniques effective in making multi-layer sheet structures can also be used.

### 35 Claims

1. A gas barrier structure for pneumatic articles, comprising a gas barrier film having low gas permeability, is characterized in that the gas barrier film is laminated between and bonded to two elastomeric surface layers and is a non-elastomeric polymeric layer that has an air permeability of no more than  $0.05 \times 10^{-10}$  cc-cm/cm<sup>2</sup>-cmHg-sec at 23° C.

40 2. A gas barrier structure for pneumatic articles, as claimed in claim 1, further characterized in that a phenolic resin is incorporated in the material of the surface layers.

3. A gas barrier structure for pneumatic articles, as claimed in claim 1, further characterized in that a tie layer is laminated between and bonded to the gas barrier film and each of the elastomeric surface layers.

45 4. A gas barrier structure for pneumatic articles, as claimed in claim 1 or 2, further characterized in that the gas-barrier film is a copolymer of vinylidene chloride (VDC).

5. A gas barrier structure for pneumatic articles, as claimed in claim 4, further characterized in that the gas-barrier film contains 60 to 95% of the VDC moiety.

50 6. A gas barrier structure for pneumatic articles, as claimed in claim 4 or 5, further characterized in that a tie layer consisting of a blend of ethylene and ethyl acrylate or other acrylate or methacrylate monomer resin and either a styrene-isoprene or a styrene-butadiene thermoplastic elastomer or its hydrogenated product is laminated between and bonded to the gas barrier film and each of the elastomeric surface layers.

7. A gas barrier structure for pneumatic articles as claimed in claim 1 or 2, further characterized in that the gas-barrier film is a copolymer of ethylene and vinyl-alcohol (EVOH).

55 8. A gas barrier structure for pneumatic articles as claimed in claim 7, further characterized in that the gas-barrier film contains less than 50 mole % of ethylene, more than 90% of the EVOH being a saponification product of ethylene-vinyl acetate.

9. A gas barrier structure for pneumatic articles as claimed in claim 4 or 5, further characterized in that the EVOH contains 2-10%, based on the weight of the copolymer, of a glycol or polyhydroxyl compound as a processing aid.
10. A gas barrier structure for pneumatic articles, as claimed in claim 7, 8 or 9, further characterized in that a tie layer consisting of a blend of maleic anhydride-grafted polypropylene and a styrene-isoprene or styrene-butadiene thermoplastic elastomer or the hydrogenated product of either is laminated between and bonded to the gas barrier film and each of the elastomeric surface layers.
11. A gas barrier structure for pneumatic articles as claimed in any of the preceding claims, further characterized in that the elastomeric surface layers are composed of thermoplastic elastomers or a blend of a thermoplastic elastomer and another synthetic or natural elastomer.
12. A gas barrier structure for pneumatic articles as claimed in claim 11, further characterized in that the elastomeric surface layers comprises a styrene block-copolymer thermoplastic elastomer.
13. A gas barrier structure for pneumatic articles as claimed in any of the preceding claims, further characterized in that the bonding between adjacent layers in the laminated structure prevents delamination when the structure is tensile-stretched to 100 percent elongation in any direction.
14. A gas barrier structure for pneumatic articles as claimed in any of the preceding claims, further characterized in that a vulcanizing agent is incorporated in the elastomeric surface layers.
15. A gas barrier structure for pneumatic articles as claimed in claim 14, further characterized in that it is the innerliner of a vulcanized tubeless pneumatic vehicle tire in which one of the elastomeric surface layers is bonded to another elastomeric layer in the tire.
16. A method for making the gas barrier structure as claimed in any of the preceding claims, characterized in that the thermoplastic polymer film and the sheets of the material used for the elastomeric surface layers are respectively prepared by extrusion or calendering to the desired thickness and the layers are laminated together to make a three-layer laminated sheet.
17. A method for making the gas barrier structure as claimed in claim 16, further characterized in that the laminated sheet is elongated beyond the elastic limit of the thermoplastic polymer film and allowed to relax to its original dimension, and is then incorporated into a tubeless pneumatic vehicle tire, and the sheet is vulcanized with the tire.
18. Use of a gas barrier structure according to any one of claims 1-15 in the manufacture of a tubeless pneumatic vehicle tire.
19. Tubeless pneumatic vehicle tire containing a gas barrier structure according to any one of claims 1-15.

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